**IMPROVEMENT OF PASSIVITY OF Fe – xCr
ALLOYS (x < 10%) BY CYCLING THROUGH THE
REACTIVATION POTENTIAL**

by

Jaganathan Ulaganathan

A thesis submitted in conformity with the requirements
for the degree of Master of Applied Science
Graduate Department of Chemical Engineering and Applied Chemistry
University of Toronto

ABSTRACT

IMPROVEMENT OF PASSIVITY OF Fe - xCr ALLOYS ($x < 10\%$) BY CYCLING THROUGH THE REACTIVATION POTENTIAL

Master of Applied Science, 2008

Jaganathan Ulaganathan

Graduate Department of Chemical Engineering and Applied Chemistry

University of Toronto

Classically 13% Cr is required for stable passivity of steel in acidic and neutral solutions not containing inhibitors. Some authors (Mansfeld, Fujimoto) have published potential cycling procedures that generate thick Cr-rich films. Fujimoto cycles right to the transpassivity potential and back in sulphuric acid solution. Our idea is to work very close to the reactivation potential where the passive film (Fe_2O_3) is reductively dissolved to Fe^{2+} . We have used an equimolar sodium acetate/acetic acid buffer, at pH 4.7. In exploring this possibility we have obtained new insights into the reactivation process itself. It is under a kind of thermodynamic control, in that the film cannot be reduced, and the metal cannot be dissolved, faster than would exceed the equilibrium concentration of Fe^{2+} at the electrode surface. Reductive dissolution leads to a gel-like Cr-rich film, but this is not protective if formed in a single step - Fe dissolution just occurs through it. However alternating formation and reductive dissolution of a Fe-rich film assist the formation of a more robust Cr-rich film.

ACKNOWLEDGEMENT

First of all, I am very grateful to Prof. Roger C. Newman for providing me an opportunity to be part of his research group. And I am indeed indebted to him to have provided excellent guidance and valuable suggestions throughout the course of my work.

I deeply thank Dr. Anatolie G. Carcea for his valuable advice towards research lab etiquettes and great assistance in my experimental work.

I would like to acknowledge financial support throughout my program from Department of Chemical Engineering and Applied Chemistry, University of Toronto; Natural Sciences and Engineering Research Council (NSERC) – Canada; and University Network of Excellence in Nuclear Engineering (UNENE).

Finally, I would like to express my gratitude to my family, friends and group members for their motivation and inspiration.

TABLE OF CONTENTS

ABSTRACT	ii
ACKNOWLEDGEMENT	iii
TABLE OF CONTENTS	iv
LIST OF FIGURES	vii
LIST OF TABLES	xiii
1. INTRODUCTION	1
2. LITERATURE REVIEW	6
2.1. Nature of passive film on Fe.....	6
2.2. Nature of Passive film on Fe-Cr alloys.....	12
2.2.1. Cr enrichment in Fe – Cr passive films	13
2.2.2. STM studies on structure of passive film	19
2.3. Passivation Models for binary alloys.....	21
2.3.1. Percolation theory.....	21
2.3.2. Graph theory	22
2.4. Passive films formed by potential cycling.....	23
3. EXPERIMENTAL DETAILS	25
3.1. Materials and working electrodes	25

3.2. Sample preparation procedures.....	25
3.3. Preparation of Electrolyte	26
3.4. Electrochemistry	26
4. RESULTS AND DISCUSSIONS	30
4.1. Electrochemistry of Fe – 8% Cr alloys in 4.67 pH acetate buffer	30
4.1.1. Potential E_p for passivation	30
4.1.2. Potential E_a for activation by selective dissolution of Fe	31
4.2. Reactivation potential of Fe	39
4.2.1. Cyclic polarization of Fe in acetate buffer	39
4.2.2. Determination of Fe reactivation potential.....	40
4.3. Cycling experiments	43
4.3.1. Effect of potential cycling on Fe – Cr reactivation from passive state.....	45
4.3.2. Effect of number of cycles	48
4.3.3. Effect of variation in E_a on Fe – Cr reactivation from passive state	49
4.3.4. Effect of Cr content on Fe reactivation	51
4.3.5. Effect of Cr content on cycling	53
4.4. Thermodynamic control of Fe reactivation in acetate buffer	54

4.4.1. Comparison of theoretically calculated Nernstian lines with experimental potentiodynamic polarization and steady state polarization	56
5. IMPLICATIONS AND FUTURE WORK.....	63
6. CONCLUSIONS	66
REFERENCES	67
APPENDIX	71

LIST OF FIGURES

Figure 1: Potential – pH equilibrium diagram for the system iron – water, at 25°C [Figure established considering Fe_2O_3] (24)	4
Figure 2: Potential in square wave form applied before passivation during cycling experiments.....	28
Figure 3: Cyclic polarization of Fe – 8% Cr between -1.0 V and 0.2 V vs. MSE in 4.67 pH acetate buffer.	31
Figure 4: Illustration of the cycling process.	33
Figure 5: Potential – pH equilibrium diagram for the system chromium – water, at 25°C [Figure established considering $\text{Cr}(\text{OH})_3$] (24).	34
Figure 6: Potential – pH equilibrium diagram for the system chromium – water, at 25°C [Figure established considering Cr_2O_3] (24).	35
Figure 7: Passivation of Fe – 8% Cr at -0.3 V vs. MSE for 30 min in acetate buffer. Two samples A and B were passivated and polarized cathodically at scan rate of 10 and 30 mV/s respectively.	36
Figure 8: Potentiodynamic polarization of Fe – 8% Cr at scan rates of 10 and 30 mV/s after passivation at -0.3 V vs. MSE for 30 min in acetate buffer.	37
Figure 9: Steady state polarization of Fe – 8% Cr from an initial passive film formed at -0.3 V vs. MSE for 30 min. Steady state current densities were measured by potentiostatic polarization at -0.45, -0.5, -0.55 and -0.6 V vs. MSE for 15 min. ...	38

Figure 10: Cyclic polarization of Fe between -1.0 V and 0.2 V vs. MSE in 4.67 pH acetate buffer.	39
Figure 11: Passivation of Fe in acetate buffer at -0.3 V vs. MSE for different durations of 30 and 195 min, prior to potentiodynamic polarization at 0.1 mV/s till -0.65 V vs. MSE.....	41
Figure 12: Potentiodynamic polarization of Fe in acetate buffer from passive state created by potentiostatic polarization at -0.3 V vs. MSE for different durations of 30 and 195 min.....	42
Figure 13: Superimposed Potential – pH equilibrium diagram for the system iron – water [considering Fe_2O_3] and chromium – water [considering $\text{Cr}(\text{OH})_3$] (shaded area) at 25°C (24).	44
Figure 14: Passivation of Fe – 8% Cr in acetate buffer at -0.3 V vs. MSE for 30 min with prior potentiostatic polarization at -0.3 V vs. MSE for 165 min (No potential cycling).	45
Figure 15: Passivation of Fe – 8% Cr in acetate buffer at -0.3 V vs. MSE for 30 min with prior polarization by potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).....	46
Figure 16: Potentiodynamic polarization of Fe – 8% Cr from passive state formed with two different prior treatments: Potentiostatic polarization at -0.3 V vs. MSE for 165 min with no cycling, Polarization by potential cycling ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min) for 5 cycles.	47
Figure 17: Final current densities of each passivation and activation step during potential cycling for 10 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).....	49

Figure 18: Comparison of steady state polarization of Fe – 8% Cr from passive film formed at -0.3 V vs. MSE for 30 min with prior potential cycling ($E_p = -0.3$ V vs. MSE for 30 min; $E_a = -0.4$ V, -0.5 V and -0.6 V vs. MSE for 3 min) along with passive film formed with prior potentiostatic polarization at $E_p = -0.3$ V vs. MSE for 165 min. Steady state current densities were measured at -0.4 V, -0.5 V and -0.6 V vs. MSE after holding potential for 60 min.....	50
Figure 19: Potentiodynamic polarization of Fe, Fe – 8% Cr and Fe – 10% Cr from passive state formed by passivation at -0.3 V vs. MSE for 30 min in acetate buffer.....	52
Figure 20: Potentiostatic polarization of Fe – 8% Cr and Fe -10% Cr at -0.6 V vs. MSE for 1 hr. Samples were passivated at -0.3 V vs. MSE for 30 min with prior polarization by either potential cycling ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min) or potentiostatic polarization at -0.3 V vs. MSE for 165 min, before measurement of steady state current density.	54
Figure 21: Potentiodynamic polarization from passive state formed by potentiostatic polarization at -0.3 V vs. MSE for 30 min, with stirring turned on and off for very short instances at random potentials.....	55
Figure 22: Potentiodynamic polarization of Pt in pH 4.67 acetate buffer	59
Figure 23: Comparison of experimental polarization data (A: Potentiodynamic, B: Steady state) for Fe reactivation with theoretical data (C: $\alpha - \text{Fe}_2\text{O}_3$, D: $\gamma - \text{Fe}_2\text{O}_3$, E: $\alpha - \text{FeOOH}$, F: $\gamma - \text{FeOOH}$, G: $\text{Fe}(\text{OH})_3$ and H: 19.5% amorphous $\gamma - \text{Fe}_2\text{O}_3$) for equilibrium relation between the different Fe^{3+} species and Fe^{2+} ions.....	61
Figure 24: Passivation of Fe – 8% Cr in acetate buffer at -0.3 V vs. MSE for 30 min with prior polarization by potential cycling for 10 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).....	72

Figure 25: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.4 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min). 73

Figure 26: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.5 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min). 74

Figure 27: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min). 75

Figure 28: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.4 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.4$ V vs. MSE for 3 min). 76

Figure 29: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.5 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.4$ V vs. MSE for 3 min). 77

Figure 30: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.4$ V vs. MSE for 3 min). 78

Figure 31: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.4 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -

0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min). 79

Figure 32: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.5 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min). 80

Figure 33: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min). 81

Figure 34: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.4 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior polarization at $E_p = -0.3$ V vs. MSE for 165 min (No cycling)..... 82

Figure 35: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.5 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior polarization at $E_p = -0.3$ V vs. MSE for 165 min (No cycling)..... 83

Figure 36: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior polarization at $E_p = -0.3$ V vs. MSE for 165 min (No cycling)..... 84

Figure 37: Potentiostatic polarization of passivated Fe – 10% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min). 85

Figure 38: Potentiostatic polarization of passivated Fe – 10% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior polarization at $E_p = -0.3$ V vs. MSE for 165 min (No cycling)..... 86

LIST OF TABLES

Table 1: Standard equilibrium potentials for different $\text{Fe}^{3+}/\text{Fe}^{2+}$ reduction reactions	57
Table 2: $\text{Fe}^{3+}/\text{Fe}^{2+}$ equilibrium potential vs. i_{lim} data for different Fe^{3+} species	71

1. INTRODUCTION

Stainless steels have a wide variety of applications in industries owing to their excellent corrosion resistance. They were developed in early 19th century after Monnartz discovered the exceptional corrosion resistance of iron – chromium alloys in aqueous solutions and humid atmosphere (1). The outstanding resistance of iron – chromium alloys to corrosion is attributed mainly to a Cr enriched passive film on its surface. It is well known that metals on exposure to any environment, not necessarily acidic or basic solution but even to open atmosphere and aqueous solutions tend to form oxide film on their surface which is thermodynamically the most stable state. The stability of these films determines the stability of the underlying metal.

Fe – Cr alloys are protected from corrosion by formation of oxides, hydroxides and/or oxyhydroxides of both iron and chromium on the surface. The composition and structure of passive film on its surface has been under scrutiny for almost a century but effort to comprehend them still continues. Even though numerous amount of work has been done, it is hard to compare different studies due to varying sample pre-treatments, passivation method and different electrochemical/analytical techniques involved. However, it is widely accepted that, passive films formed in electrolytes are more protective than air formed oxide films. Also the influence of passivation potential, time and electrolyte composition on chemical composition and thickness of passive film formed under an applied field is well established.

Passive films on Fe – Cr alloys formed in several electrolytes with a wide range of pH have been studied. In all the studies, Cr enriched passive film was determined to be

formed on the surface (2-13). Though the extent of enrichment varies between studies, the most widely accepted reason for such enrichment is selective dissolution of Fe as Fe^{2+} into the solution at primary passivation potentials (6-8, 12, 13). Another theory explaining Cr enrichment is the stability of Cr oxides in acidic solutions and low mobility of Cr cations compared to Fe cations within inner layers of the passive film (7, 9, 14). Even though Cr enriched passive film is known to enhance the passivity of Fe – Cr alloys compared to pure Fe, role of Cr in passivation mechanism and protectiveness of the passive film are still wide open to be studied. A major drawback in studying Cr enrichment is the extreme thinness of passive films which is often in the order of few tens of Å. Limitations in analytical techniques available for surface analysis within an electrolyte is another huge drawback.

Another interesting fact is that Fe – Cr alloys become truly stainless, i.e., attain complete passivity only above a 13% Cr threshold in acidic solutions (15). Many studies have shown that below ca. 10% Cr, properties of iron are dominating and above ca. 15% Cr properties of Cr are dominating in the alloy. Electrochemical studies have shown evidence for sharp transitions for reactivation at 13% Cr for films formed at complete passivation potentials (where both Fe and Cr oxidize) and at 17% Cr for films formed at primary passivation potentials (where only Cr oxidizes) (16). Structural studies using Scanning Tunnelling Microscopy (STM) have shown that structural stability and rigidity of the initially disordered passive film increases above 17% Cr (17, 18).

Numerous works have been carried out to interpret this threshold behaviour of Fe – Cr alloys based on passivation models. There are basically two classes of models which could possibly explain the threshold behaviour. Uhlig (19) was the first to quantify passivation based on an electronic model. He predicted transitions in behaviour at 15.7 % Cr.

But the use of this electronic model to interpret the threshold behaviour lacked conviction as it used bulk electronic properties to explain passivation which is actually a surface phenomenon. Geometrical models like Percolation theory by Seiradzki and Newman (20), Graph theory by McCafferty (21) explain passivity based on geometrical arrangement of passive film on the surface. These models require an infinite network of --Cr--O--Cr-- chains to completely cover the surface to prevent further dissolution of Fe atoms.

Though the 13% threshold is well established, this present work aims to improve Fe – Cr alloys with lower Cr content ($\leq 10\%$). Formation of Cr enriched passive film by selective dissolution of Fe forms the basis of this study. It is well known that passive films act as a barrier to subsequent dissolution of underlying metal. The problem with low Cr alloy is that, if the passive film is formed in a single step, it is highly disconnected because of non – availability of sufficient Cr atoms to achieve complete coverage, due to which their barrier capacity is compromised. So if we could somehow continually make removal of Fe atoms from the surface possible, to the point of complete surface coverage by --Cr--O--Cr-- links, robust Cr enriched films can be obtained. Also passive films formed on Fe surface is known to be removed by reductive dissolution resulting in Fe reactivation (22, 23).

Therefore, our hypothesis is that cycling through the reactivation potential will continually enrich the film in Cr until the low-Cr alloy starts to behave like a stainless steel. Therefore the key issues addressed in this work include

1. Determination of reactivation potential on Fe and Fe – Cr alloys in pH 4.7 acetate buffer.
2. Effect of cycling through reactivation potential on Fe – 8% Cr and Fe – 10% Cr.

During the studies on Fe microelectrode, it was noticed that reactivation of Fe from passive state follows an inverted tafel behaviour. So the thermodynamic implications have been explored gaining insights into the reactivation process. The possible thermodynamic control on Fe reactivation is illustrated in the Pourbaix diagram for Fe – water system shown below. The current limitation at each potential due to finite concentration of Fe^{2+} in equilibrium with Fe_2O_3 is clearly evident at pH 4.7, i.e., the rate of reductive dissolution of passive film on the surface should be controlled by its solubility in the solution.

Figure 1: Potential – pH equilibrium diagram for the system iron – water, at 25°C [Figure established considering Fe_2O_3] (24)

Since Fe reactivation occurs by reductive dissolution of Fe^{3+} oxides/oxyhydroxides into solution as Fe^{2+} ions, the thermodynamic control could possibly mean a mass transport control based on diffusion of Fe^{2+} ions into the bulk. So, theoretical calculations using Nernst equation and limiting current based on mass transport control have been made to understand the nature of passive film on Fe.

In this study, only preliminary electrochemical work has been undertaken to check the feasibility of our hypothesis. In the forth coming sections, relevant literature on nature of passive film on Fe – Cr alloys and Fe have been dealt in Chapter 2. Also some structural studies and passivation models validating the studies on nature of passive film have been included. Chapter 3 elaborates on sample preparation and deals with the experimental procedures utilized to study the key issues mentioned above. The results obtained and their implications are discussed in Chapter 4. The implications of this present work and recommendations towards future work are mentioned in Chapter 5. Finally some conclusions have been drawn in Chapter 6 which is followed by sections on References and Appendix.

2. LITERATURE REVIEW

2.1. Nature of passive film on Fe

The nature of passive film on Fe has been under study for centuries now. Still there are disagreements regarding the composition of the film as to being a single or duplex layer or a single layer with gradient along film thickness. But the widely acknowledged theory is that of a bi-layer passive film with Fe_3O_4 forming the inner layer and the outer layer could be either $\alpha - \text{Fe}_2\text{O}_3$, $\gamma - \text{Fe}_2\text{O}_3$ or $\gamma - \text{FeOOH}$ depending on passivation conditions.

In particular, extensive work by Cohen et al. for more than three decades from late 1950's has provided valuable knowledge on electrochemical aspects of passive films on Fe. Nagayama and Cohen (25) studied passive films formed by anodic oxidation of Fe in pH 8.4 borate buffer. They used cathodic reduction technique and electron diffraction to study the thickness and composition of the passive film as a function of applied anodic potential. Through the determination of Fe^{2+} ions in solution by colorimetric techniques, they deduced the amount of charge present in the film and thereby its thickness. By analyzing the passive film at intervals during the cathodic reduction, using electron diffraction, they determined it to be a bi-layer with Fe_3O_4 inner and $\gamma - \text{Fe}_2\text{O}_3$ outer layers. At lower passivation potentials magnetite covers most parts of the surface and with increase in potential surface coverage reaches 100% and $\gamma - \text{Fe}_2\text{O}_3$ forms on top of magnetite. Also they noticed evidences for vacancy structure in the electron micrographs and assumed the outermost layer to be a cation defect structure of $\gamma - \text{Fe}_2\text{O}_3$.

In another part of the same study (26) they studied the effect of Fe^{2+} concentration on anodic oxidation of iron. They identify a potential which separates the passive region into two, below which Fe dissolution into solution as Fe^{2+} ions is evident and above which there is no detectable Fe^{2+} formation in solution. Also they determined that the excess Fe^{2+} ions in solution over the equilibrium value oxidize to form $\gamma - \text{Fe}_2\text{O}_3$ resulting in growing films unlike in ferrous ion free solutions where the film attains a maximum thickness.

Later Markovac and Cohen (27, 28) determined that oxides formed by anodic oxidation of iron and anodic deposition from aqueous solution containing dissolved Fe^{2+} ions differed both in chemical composition and electrochemical properties. To minimize complications from simultaneous oxidation and reduction, Pt substrates were used instead of Fe. Passive films formed by anodic deposition led to incorporation of anions and water molecules into the film. The weight of the deposited film was 60 – 90 % more than that could be expected from a $\gamma - \text{Fe}_2\text{O}_3$ film. But a mixture of hydrated iron ($\text{FeOOH} \cdot \text{H}_2\text{O}$) and boron oxides possibly explained the weights observed. Also their efforts to remove water by heating in vacuum resulted in transformation of $\gamma - \text{FeOOH}$ to $\alpha - \text{Fe}_2\text{O}_3$.

Borate ions being strong complexing agents, perchlorate solutions were used to anodically oxidize dissolved Fe^{2+} ions with and without additions of anions like phosphates, sulphates, acetate and chloride to study the effect of their presence in solution (29). In all cases $\gamma - \text{FeOOH}$ was observed on the surface and only phosphate ions were found to be incorporated in the film from electron diffraction and chemical analysis.

From these detailed studies Cohen (30) concluded that anodic oxidation of iron forms a anhydrous Fe_3O_4 inner and $\gamma - \text{Fe}_2\text{O}_3$ bi-layer on the surface and the presence of Fe^{2+} ions

in solution either by deliberate addition or from Fe dissolution depending on how the Fe is brought to the passivation potential forms additional γ – FeOOH outer film with incorporation of Fe^{2+} , water molecules and certain anions like borates and phosphates on the surface.

Foley and Kruger et al. (31) carried out electron diffraction studies of prepassive, passive and transpassive oxide films formed on different orientations of Fe substrate in H_2SO_4 of pH 1.1, borate buffer of pH 8.5 and NaOH of pH 11.4 solutions. They noticed the oxide composition to show dependence on orientation of surface but not on pH of solution. Also they identified the surface of the films as γ – Fe_2O_3 in the passive region and as Fe_3O_4 in prepassive and transpassive regions in all solutions. They postulate that the very low conductivity of γ – Fe_2O_3 differentiates it from highly conductive Fe_3O_4 and leads to the passive state of the metal. Further, Kruger et al. (32) studied the thickness of the film using a non – electrochemical technique, Ellipsometry, and inferred from the kinetics that the outermost part of the film formed in borate buffer to be a poor conductor.

Under similar conditions of passivation as used by Cohen, Sato et al. (33, 34) project the passive film to be a single phase of hydrous ferric oxide. Their cathodic reduction studies depict simultaneous reductive dissolution of the oxide as Fe^{2+} ions and reduction to a lower oxide which later gets reduced to Fe. Thus they conclude that the lower oxide (Fe_3O_4) in the bi-layer model of Cohen et al. to be not formed by oxidation of the substrate iron but by solid state reduction reaction of γ – Fe_2O_3 during cathodic reduction. But unlike Cohen et al., the cathodic reduction was carried out at a lower pH of 6.35 and current density of $5 \mu\text{A}/\text{cm}^2$ instead of pH 8.5 and $10 \mu\text{A}/\text{cm}^2$. And at such low pH values, Oswin and Cohen (23) have shown Fe dissolution to possibly mislead interpretations from cathodic reduction results.

Bardwell and Graham et al. (35) studied the nature of passive film on Fe in ^{18}O enriched borate buffer by galvanostatic cathodic reduction in conjunction with ^{18}O – SIMS. SIMS measurements with depth confirm uniform layer by layer removal of the film rather than patch-wise reduction exposing metal surface. The rate of decrease in thickness showed two distinct linear regions depicting two mechanisms during cathodic reduction. The amount of charge passed during each region was comparable to theoretical rate of reduction of $\gamma - \text{Fe}_2\text{O}_3$ to Fe^{2+} and Fe_3O_4 to metallic Fe from which they concluded the outer layers to be $\gamma - \text{Fe}_2\text{O}_3$ and inner layers to be either Fe_3O_4 or $\gamma - \text{Fe}_2\text{O}_3$ incorporated with ferrous ions. Fe_3O_4 being a mixed oxide of ferric and ferrous ions, they attribute the change in mechanism to the exposure of ferrous ions during cathodic reduction.

The doubts on stability of films to ex-situ analysis have led to more recent studies being carried out with in-situ techniques. X – Ray Absorption Spectroscopy (XAS) is one of the very few techniques available for making structural and compositional studies of metals and alloys in-situ within an aqueous solution. Generally these in-situ techniques require thin film samples made by sputter deposition. Most of the authors have shown that results from thin film samples are significantly similar to bulk alloys. The only difference being lower current densities owing to lower surface roughness (1, 11, 36).

The XANES spectra for $\alpha - \text{Fe}_2\text{O}_3$, $\alpha - \text{FeOOH}$ and $\gamma - \text{FeOOH}$ always show a characteristic split pre-edge peak unlike a single pre-edge peak exhibited by Fe_3O_4 and $\gamma - \text{Fe}_2\text{O}_3$. This difference is attributed to the presence of tetrahedral co-ordinated Fe in the literature. Davenport et al. (37) studied passive films formed on thin film of Fe (100 Å) in pH 8.4 borate buffer using XANES and noticed a single pre-edge peak on the passive film

spectrum, which limits the components of the passive film that can be possibly present to $\alpha - \text{Fe}_2\text{O}_3$, $\alpha - \text{FeOOH}$ and $\gamma - \text{FeOOH}$.

In another work (38), they followed the galvanostatic reduction of passive film formed on 40 Å and 100 Å Fe films under same conditions with XANES. They noticed a steady decrease in edge height with time implying layer by layer removal of the oxide film as observed by Bardwell et al. (35) with SIMS. They also noticed the shift in edge height to be characteristic of a change from $\gamma - \text{Fe}_2\text{O}_3$ to that of Fe_3O_4 , by comparing edge heights of standards of oxide compounds. The thickness of film plays significant role as thin films get oxidized entirely while some metallic Fe might still remain underneath the oxide in case of thicker films emitting signals.

The potential dependence of Fe passivation in pH 8.4 borate buffer was studied by Oblonsky et al. (39) with 50 Å thin films using XANES. They identified from a drop in edge height of the XANES spectra, a critical potential of -600 mV vs. MSE below which Fe dissolution occurs along with passivation; which corresponds to the -200 mV vs. SCE observed by Cohen et al. (25) by chemical analysis of the solution during passivation. Also they noticed only a drop in edge height at lower passivation potentials but not a decreasing edge height suggesting Fe dissolution to occur only at initial stages and not through the film during passivation. Since XANES spectra gives only the average valence of Fe in the passive film without depth resolution, they suggest that the oxide film could possibly be made of Fe^{3+} ions with some Fe^{2+} ions whose concentration changes with potential and not a bi-layer as inferred in previous XANES studies. In this study they measured a gradual change in Fe^{2+} ion concentration from $7 \pm 3\%$ at 400 mV to $17 \pm 3\%$ at -800 mV. Also they observed the critical potential above which there is no detectable Fe dissolution to increase with increase

in pH and concentration of solution. But there was no change in composition of film with pH and concentration.

Most work on Fe passivation have been carried out in pH 8.4 borate buffer, as it does not exhibit detectable Fe dissolution at passivation potentials and prevents local changes in pH at the surface which could possibly alter passivation mechanism. Only few studies have been carried out in acetate buffer.

Takahashi and Graham et al. (40) studied the anodic and cathodic behaviour of Fe in acetate buffer. They studied cathodic reduction of films, formed in pH 7 acetate and pH 8.4 borate buffers, in both solutions by comparing the charge passed during two potential arrests of galvanostatic reduction. The reduction of films formed in pH 8.4 borate buffer at 0.4 V vs. MSE, in both acetate and borate buffers of pH 7 were very similar except at acetate concentrations ≥ 0.5 M, where possible complexing effects change the mechanism drastically. But by increasing pH of solutions with higher acetate concentration they obtained relatively comparable results. The reduction of films formed in pH 7 acetate buffer (acetate concentration ≥ 0.1 M) at 0 V vs. MSE in pH 7 acetate (acetate concentration ≤ 0.1 M) and pH 8.4 borate buffers were similar. From these results they concluded that films formed in neutral acetate buffer with concentrations more than 0.1 M follow the $\text{Fe}_3\text{O}_4/\gamma - \text{Fe}_2\text{O}_3$ bi-layer model.

Oblonsky et al. (41) studied formation of passive films, on Fe in acetate buffer at different pH values between 4.5 and 7.5, and their galvanostatic reduction using in-situ XANES. They identified that, characteristics of passive films formed under different conditions were essentially the same. The thickness of film and their oxidation states were

more or less identical, and independent of pH. But the galvanostatic reduction of passive film was highly dependent on pH. Also they identified that, the passive film was not completely removed by reductive dissolution of Fe_2O_3 to Fe_3O_4 and metallic Fe. At low pH of 4.5, they proposed the electrochemical dissolution of oxide to be accompanied by chemical dissolution of Fe_3O_4 as well; and accelerated by autocatalytic reduction with the help of excess electrons created by Fe dissolution through discontinuities formed during reduction. The observed charge densities during galvanostatic reduction could not directly support $\text{Fe}_3\text{O}_4/\gamma - \text{Fe}_2\text{O}_3$ bi-layer model of passive film. But with the inception of chemical dissolution and autocatalytic reduction they were able to rationalize it.

With sufficient information on formation of passive film on Fe and their solution dependent characteristics, passive films on Fe – Cr alloys are discussed next.

2.2. Nature of Passive film on Fe-Cr alloys

Fe – Cr alloys have been studied by several authors over the years. They have gained such technical importance because of their outstanding corrosion resistance, in particular, at negative potentials where they show improved passivity compared to Fe because of their tendency to form oxides at more negative potentials. Passivation of Fe – Cr alloys in acidic solutions have gained further significance as they exhibit sharp threshold behaviour at 13% Cr under these conditions.

Good understanding on the protectiveness of the passive film on Fe – Cr alloys over Fe, requires good knowledge of composition and structure of the passive film. It is widely accepted that Fe – Cr forms a porous amorphous film on the surface. And in acidic solution it is believed to be a bi-layered film with Cr^{3+} and Fe^{3+} oxides forming the inner layer enriched

with Cr_2O_3 and chromium hydroxide or oxyhydroxide outer layer (9, 10, 13). The excellent corrosion resistance of Fe – Cr alloys compared to pure Fe is believed to be mainly due to this Cr enriched passive film. Several studies have been undertaken to understand the Cr enrichment using various ex-situ techniques such as Auger Electron Spectroscopy (AES), X-Ray Photoelectron Spectroscopy (XPS), Ion Scattering Spectroscopy (ISS) and in-situ techniques such as Mossbauer Spectroscopy, X-Ray Absorption Near Edge Spectroscopy (XANES), X-Ray Absorption Fine Structure (EXAFS). But the degree of enrichment has not been quantified yet. The thickness of each layer and extent to which Fe and Cr oxides and ions are present in each layer depends upon the passivation conditions.

2.2.1. Cr enrichment in Fe – Cr passive films

Lumsden and Staehle (2) were the first to show the utility of AES along with ion sputtering to study composition gradient in thin films formed on metal surfaces. They analysed Type 316 stainless steel and noticed Cr enrichment in the film. One of the first studies on composition of passive film on Fe – Cr alloys using AES was carried out by Yaniv et al. (3). They determined Cr enrichment in the passive film to increase with increase in Cr content of the bulk alloy. Fe – Cr – Mo alloys with 13, 17 and 25% Cr was studied in acidic solutions with pH ranging from 2 to 3.45. They also noticed that unlike electrochemically formed passive films, the ones formed chemically in HNO_3 did not show any dependence on bulk Cr content for Cr enrichment in the passive film, which could possibly imply on the selective dissolution of Fe under electrochemical control leading to Cr enrichment as explained later by several authors.

The dependence of composition and thickness of passive film on passivation potential and time was studied by Mitrovic – Scepanovic et al. (4) in the early 1980's. Fe – 26% Cr was passivated in de-aerated pH 2 sulphuric acid and they noticed that the thickness of the film to be independent of potential and time but the dependence of Cr enrichment was evident. Their quantitative AES shows higher degree of Cr enrichment in the inner layer compared to outer layer at negative potentials, and a diminishing difference in between layers with increasing potential. Also the Cr enrichment in the film increases towards anodic potentials. They also show the importance of cathodic pre-treatment of the surface prior to passivation. They found thickness of the film to be dependent on potential when the air formed films were not removed. Also they noticed Cl^- incorporation (from their electropolishing of samples prior to passivation) into the passive film when the surface was not cathodically reduced.

The capability to determine the valence state of elements has given XPS a slight edge over AES. Olefjord and Fischmeister (5) utilized XPS to analyse passive film composition on Fe – Cr alloys in early 1970's. Cr enrichment was noticed by them on the surface reaching even 100% over long exposure to oxygenated water. Asami et al. (6) used this method to study the passive film on Fe – Cr alloys formed in sulphuric acid. A wide range of alloy composition from 10% to 80% Cr was studied in 1 M H_2SO_4 at potentials of 100 mV and 500 mV vs. SCE. In all the alloys Cr enrichment in the passive film was evident except for Fe – 10% Cr at 100 mV where the alloy is still active. Also they noticed that the metal surface directly beneath the film was not enriched in Cr and that the air formed films were not enriched in Cr. Furthermore, they show transitions in binding energies of Fe $2\text{P}_{3/2}$ and O

1S electrons at ca. 13% Cr to elucidate on the threshold property of ferritic steels at 13% Cr to achieve complete passivation.

Most of the studies on Fe – Cr alloys were conducted with > 10% Cr content. Cr enrichment with alloys less than 13% Cr was shown by Kirchheim et al. (7). They studied Fe – Cr samples with Cr content in the bulk ranging from 0.6% to 18% in 1 N H₂SO₄. Their XPS study showed a Cr enrichment gradient decreasing within the passive film towards the metal surface unlike Mitrovic – Scepanovic (4) whose AES studies showed the gradient in the opposite direction. Kirchheim et al. explain the overall Cr enrichment in the film as a result of selective dissolution of Fe in the outermost layers and lower mobility of Cr cations compared to Fe cations from within the subsequent inner layers. Though the Cr enrichment is the most when Cr content of the bulk alloy is the most, Kirchheim et al. define an enrichment factor (Cr in passive film to Cr in bulk alloy) which reflects on the degree of enrichment in the passive film. And degree of enrichment is the most for alloy containing least Cr content. But they did not notice any abrupt changes associated with the 13% threshold except for a change in critical current density for passivation. This might be because of the maximum Cr content studied by them being 18% and not much difference might have been noticed from 13% to 18%.

The difference in Cr enrichment gradient within the passive film between studies carried out by Kirchheim et al. (7) and Mitrovic – Scepanovic (4) maybe explained based on the time spent for passive film formation. Haupt and Strehblow (8) obtain higher Cr enrichment in the inner layers like Mitrovic – Scepanovic but predict that with longer durations in the order of weeks would probably remove more Fe by selective dissolution leading to comparatively higher degree of Cr enrichment in the outer layers. They observed

that passivation of Fe – 15% Cr showed an increase of Cr content in the passive film from 30% to 57% for an increase in time from 10 s to 3 hr. Haupt and Strehblow studied Fe – 15% Cr and Fe – 20% Cr in 0.5 M H₂SO₄ using electrochemical techniques with Rotating Ring Disc Electrodes (RRDE) as well as XPS and ISS to gain insights into the passivation of these alloys. They also observed that pre-treating the sample at a slightly negative potential near active region for a very short duration before passivation at more anodic potentials would result in higher Cr enrichment within the film.

Maurice et al. (9) studied Cr enrichment at atomic scale in Fe – 22% Cr (110) single crystals. Their XPS analysis did not record any Cr enrichment in the air formed oxide films as shown previously by Asami et al. (6) using AES. The air formed oxide films follow stoichiometry of the bulk alloy. Passive film was formed on the single crystals in 0.5 M H₂SO₄ for various exposure times and passivation potentials. In all cases Cr enrichment is evident and they determine that the passive film has an outer layer made of 100% Cr(OH)₃ which is contrary to results from Mitrovic – Scepanovic (4) but similar to results from Kirchheim et al. (7). Maurice et al. reason that exposure to air during transfer from electrochemical experimental setup to Ultra High Vacuum (UHV) chamber of XPS or AES technique (Kirchheim et al. used a closed transfer unit unlike Mitrovic – Scepanovic who transferred in open air) might possibly lead to formation of iron oxides or re-precipitation of Fe species on the surface.

Recent work by Keller and Strehblow (10) using a closed chamber for transferring specimens to and from the electrolyte and the UHV show that lower valent species like Fe²⁺ are preserved within the film and that uncontrolled oxide growth are prevented by preventing exposure of specimen to air. They passivated Fe – 15% Cr and Fe – 20% Cr in 0.5 M H₂SO₄

at several potentials between pre-passive and transpassive potential regions for 300 s at each potential. Cr enrichment is clearly evident, but they show mainly Cr(OH)_3 in the outer layer along with minor fraction of Fe^{2+} in pre-passive region and a bi-layer model containing chromium hydroxide outer part and mixed Fe and Cr oxide inner part along with Fe^{2+} in the passive region. Generally lower valent species are not detected in the passive region but they noticed Fe^{2+} in the passive film till 0.9 V vs. SHE and hypothesize that either it is trapped in the film or forms a complex oxide like chromite (FeCr_2O_4) which is stable in acidic solutions.

Over the years several authors have debated on the validity of ex-situ surface analysis. Secondary Ion Mass Spectroscopy (SIMS) in conjunction with ^{18}O - labelling has been carried out by Bardwell et al. (42-45) on Fe and Fe – Cr alloys; and they have determined that the ex-situ stability of passive film decreases with increasing Cr content. Even though Kirchheim et al. (7), Haupt and Strehblow (8) and Marcus et al. (9) have utilized a closed transfer chamber in their work to eliminate exposure to air, still there are concerns over possible dehydration effects, localized heating when subjected to ion sputtering and loss of electrochemical control when transferring from aqueous environment to UHV.

XAS was used for in-situ studies on bulk metals and thin films from early 1980's, but those studies demonstrated only changes in absorption spectrum with passivation. Kerkar et al. (11) were the first to perform in-situ structural studies using EXAFS and XANES to determine structural information on Fe and Fe – Cr alloys in borate buffer and perchloric acid. They determined that Fe is in the form of γ – FeOOH in passive films on Fe and Fe – Cr alloys. Previous ex-situ studies determined γ – Fe_2O_3 to be the major constituent of

passive film under these conditions. They hypothesize that $\gamma - \text{Fe}_2\text{O}_3$ can transform into $\gamma - \text{FeOOH}$ at elevated temperatures which is highly possible when exposed to electron beams and underlined the importance of in-situ studies. Also Cr was shown to be present mainly in the form of $\text{Cr}(\text{OH})_3$ unlike Cr_2O_3 as observed in ex-situ studies.

Later Davenport et al. (12) applied in-situ XANES to study passive film chemistry on Fe – 26% Cr in pH 8.4 borate buffer. They observed from Fe and Cr K – edges that both Fe and Cr were oxidized into the film while stepping to 0.4 V vs. MSE and while stepping back to -1.5 V Fe was lost by reductive dissolution and Cr was enriched in the film. Oblonsky et al. (13) made an effort to study Cr enrichment in a wide range of alloy composition from 8.5% Cr to 23% Cr in pH 4.5 acetate buffer. Previous studies being mainly qualitative, they made a quantitative study on the passive film composition. They determined that Cr enrichment ranged from 4 to 7 times the alloy composition when passivated at lower potential regions (ca. -300 mV vs. MSE) and 2 to 3 times when passivated at higher potential regions (ca. 200 mV vs. MSE). Like Kirchheim et al. (7) maximum Cr enrichment was observed in low-Cr alloys.

In general, Cr enrichment is noticed at all conditions of passivation. But the work of Kirchheim et al. (7) and Obonsky et al. (13) is significant towards this present study as they have shown Cr enrichment even in low-Cr alloys and that the degree of enrichment to be the maximum for low-Cr alloys. Another significant work towards this study is that of Haupt et al. (8) who have shown improvements in passive film when pre-treated at slightly negative potentials. The most pertinent work is that of Davenport et al. (12) where they cycle between anodic and cathodic potentials. Though their intention for cycling was to study transpassive

dissolution of Cr^{6+} , by changing the potentials for cycling Cr can be retained in the film leading to a robust Cr enriched passive film.

2.2.2. STM studies on structure of passive film

Apart from the chemical composition of films formed on Fe – Cr surfaces their structure too is important to elucidate on its corrosion properties. Several techniques have been utilized for these structural studies such as Electron Diffraction (ED), EXAFS and Scanning Tunnelling Microscopy (STM). McBee and Kruger (46) were the first to undertake structural studies on Fe – Cr alloys using ED. They found that amorphous films resulted in higher Cr content alloys where as spinel type crystalline structure resulted in the case of $\leq 10\%$ Cr alloys. And the amorphous nature of film was taken to be providing excellent corrosion resistance properties. STM has now given the ability to study surfaces with atomic resolution and a few prominent studies have been discussed below.

Ryan and Newman et al. (17, 18, 36) have carried out a series of in-situ and ex-situ STM studies on structure of passive films. They studied films formed on sputter deposited Fe – Cr surfaces in 0.1 M H_2SO_4 . They noticed a distorted triangular lattice in alloys with wide range of Cr content. In some cases they even noticed ring structures beneath the triangular lattice and consider that as an indication of bi-layer structure of CrOOH on Cr_2O_3 . Low Cr alloys (13 to 15% Cr) were found to form highly crystalline films whereas higher Cr content alloys resulted in more or less amorphous films. Based on Percolation theory they speculated that, in the case of low Cr alloys, the Cr atoms have to structurally relax to form oxygen bonds with neighbouring Cr atoms. In the process they undergo electrochemical polymerization of CrOOH resulting in atomic order. Alloys with $\geq 17\%$ Cr (Percolation

threshold), forms highly connected film instantly and retain disorder but with high stability as dissolution of hydrated cations through the continuous network is very difficult. Also they observed higher structural stability of films in the case of in-situ studies.

Marcus et al. (9, 47) systematically studied the passive films formed on single crystals of Cr and Fe – 22% Cr alloy using ex-situ STM. On both Cr and Fe – 22% Cr surfaces, a step and terrace topography was observed in the microscopic level. No long range order, but only disordered arrangement of nanoscopic protrusions was observed on Cr surface which were attributed to islands of Cr_2O_3 protruding through CrOOH terrace. In atomic scale, they observed ordered corrugations with trigonal symmetry on the terraces similar to triangular lattice attributed to CrOOH by Ryan and Newman (17) on Fe – Cr surfaces. On ageing they observed an increase in the ordered domains and attributed it to growth of oxide nanocrystals at the metal/film interface. They also propose that, flexible structure of hydroxide fills the gap in oxide nanocrystals thereby preventing their breakdown.

In the case of Fe – 22% Cr surface (9), step and terrace topography was observed both before and after passivation. In the microscopic scale, they observed platelets on the terraces of passivated surface which they attributed to non-corroded / Cr enriched areas. At more positive potentials the larger platelets were formed which was inferred as dissolution of areas surrounding the non-corroded / Cr enriched areas. Similar to Cr surface, nanoscopic protrusions were observed on the alloy. But unlike in Cr, fusing of protrusions was observed with time under potentiostatic polarization. Passive films on both Cr and Fe – Cr are formed by nucleation and growth process. So the fusing of protrusions was inferred by them to be made plausible because of selective dissolution of Fe^{3+} making way for coalescence of oxide nanocrystals.

2.3. Passivation Models for binary alloys

There are several theories explaining passivity, in particular trying to explain the drastic transition in properties of Cr containing alloys beyond 13% Cr. Uhlig (19) was the first to explain passivity based on an electronic model. He reasoned electronic configuration to play in the passivation of transition metal alloys at specific compositions. In the case of Fe – Cr alloys, eliminating d – electron configurations characteristic of Fe atoms would make them electrochemically indistinguishable from Cr atoms. Based on which, a 15.7% Cr threshold was predicted by Uhlig. As mentioned earlier, this utilizes bulk electronic properties to explain surface passivation which lacked conviction. Several other workers tried explaining passivity based on kinetics. But the independence of this transitional behaviour on alloy composition (except Cr content) and temperature has recently led to rise of geometrical models explaining passivity. The most prominent geometrical models – Percolation theory and Graph theory are discussed below.

2.3.1. Percolation theory

Newman and Sieradzki (20) proposed a percolation model explaining passivity of alloys in 1986. This model necessitates a threshold concentration of atoms of passivating element to be present in the original alloy. In the case of Fe – Cr alloys, they explain that passivation occurs by blocking of ledges, exposed by selective dissolution of Fe, with –Cr–O–Cr– oxide or oxyhydroxide chains, thereby suppressing further Fe dissolution. For this to materialize, a threshold concentration of Cr atoms is required for infinite connectivity at or very close to their original lattice positions without movement. Since formation of CrOOH does not require Cr atoms to be immediate neighbours, they simulated a threshold of

17.5% Cr (in the alloy) for interactions of 1st and 2nd neighbours; whereas 9.5% Cr was found to be sufficient to achieve infinite connectivity if 3rd nearest neighbours were also involved.

However, this does not explain the essential 13% Cr threshold required to become stainless. They proposed the 13% Cr threshold to be a reactivation threshold instead of passivation threshold. Electrochemical studies by Fujimoto (16) have shown transitions at 10% Cr and 17% Cr as predicted by percolation theory, corresponding to passivation at complete passivation potentials and primary passivation potentials of Fe – Cr alloys respectively. Only during reactivation from passive state, obtained at complete passivation potentials, they notice a transition at the traditional 13% Cr. Recently, in-situ X – Ray fluorescence microprobe studies by Davenport et al. (1) found transitions at 17% Cr content, above which very little dissolution was detected and below which dissolution of both Fe and Cr was detected. This 17% threshold is consistent with the percolation model for passivation.

Also, based on percolation theory, Fe – Cr alloys with $\leq 10\%$ Cr should form clusters of Cr oxide that do not have infinite connectivity, some of which would be lost just by selective dissolution of surrounding Fe atoms. This was evidenced by experiments that resulted in greater mass loss on 8 – 12% Cr alloys when compared with anodic charge actually passed (48).

2.3.2. Graph theory

McCafferty rationalised passivity based on another mathematical model – Graph theory (21, 49). Percolation model by Newman and Sieradzki assumed passive film to be purely made of Cr³⁺ ions bridged by O²⁻ links. Contrary to that, chemical and structural analysis have shown Fe³⁺ ions to be a constituent of passive films on Fe – Cr alloys. Using

graph theory, McCafferty follows similar logic as percolation theory in forming a connected --Cr--O--Cr-- network on the surface; but follows it up by randomly substituting Cr^{3+} ions with Fe^{3+} ions in the oxide film. The critical concentration of Fe^{3+} at which Cr^{3+} ions lose their infinite connectivity is determined. This is then correlated to the atomic fraction of Cr in the alloy. For Fe – Cr alloys, McCafferty estimated a 70% Fe^{3+} ion concentration, which conversely means 30% Cr^{3+} ions in the oxide film leading to passivity. The 30% Cr^{3+} ions in the oxide correspond to 13% Cr content in the alloy. The correlation being mainly based on a XANES study by Oblonsky et al. (13) to determine Cr enrichment in oxide film on Fe – Cr alloy. McCafferty with help of Graph theory, has explained threshold behaviour in several binary alloy systems like Cr – Mo, Cr – Zr, and some non-Cr binary alloys like Mo – Ti (50). One particular assumption to be noted is a uniform composition of passive film with depth, even though there are several studies showing gradients in composition.

2.4. Passive films formed by potential cycling

Generally passive films are formed by potentiostatic polarization at potentials in the region of passivity of material involved. Mansfeld et al. (51-53) utilized an Alternating Voltage (AV) passivation process to form modified surface films resulting in enhanced corrosion resistant properties. They studied the effectiveness of AV passivation over DC passivation on Type 304 stainless steel in 0.5 M H_2SO_4 . In the AV passivation, potential in a square wave form was applied for the same duration as in DC passivation. They varied the amplitude and pulse width of the square wave to determine optimized conditions to achieve highly stable passive films. They observed that, films formed by AV passivation showed higher resistance to attain OCP of bare metal on removal of electrochemical control. They also achieved reductions in passivation current densities and critical current densities. They

explained the improvement to be caused by possible dehydration of chromium hydroxides resulting in more stable $\text{CrOOH/Cr}_2\text{O}_3$ film on the surface. Also Schmuki and Mansfeld et al. (54) observed an increase in photocurrents from passive films formed by AV passivation. They inferred the results as formation of thicker films by AV passivation and possible removal of structural defects based on a semiconductor model of passive film.

Fujimoto et al. (55, 56) studied formation of thick coloured passive films on Type 304 stainless steel using square wave potential pulse polarization in 0.5 M and 5 M H_2SO_4 . They observed that by choosing higher (E_H) and lower (E_L) potentials of the pulse in active, passive or transpassive regions of Cr; thickness of passive film and thereby interference colour could be controlled. They proposed several mechanisms to explain observed experimental data. They observed that by choosing E_L in active region and E_H in passive region, linear film growth could be obtained; and proposed anodic dissolution of Fe^{2+} , Cr^{2+} at E_L followed by anodic oxidation of Cr^{2+} to Cr^{3+} at E_H . Also they observed that by choosing E_L in passive region and E_H in transpassive region, Cr^{6+} formed by transpassive dissolution at E_H was cathodically reduced to Cr^{3+} at E_L . Though thick films were obtained by both mechanisms they observed them to be susceptible to pitting due to their highly porous nature.

In both the studies, the potential was alternately stepped between different potentials. This procedure is termed as potential cycling in this study and has been applied to form robust Cr – enriched passive films on Fe – Cr alloys. In the next sections, the experimental details regarding potential cycling and their results are discussed in detail.

3. EXPERIMENTAL DETAILS

3.1. Materials and working electrodes

Fe, Fe – 8% Cr, Fe – 10% Cr samples were used in this study. 250 μm Fe wire with a purity of 99.998% was obtained from Alfa Aesar. Fe – 8% Cr and Fe – 10% Cr were obtained from UMIST, Manchester, UK. The alloys had undergone hot rolling treatment and their final condition as-rolled was around 350 μm thickness sheets.

3.2. Sample preparation procedures

Fe wire was used as received from manufacturer. Bulk Fe – Cr alloys were cut into approx. 5 mm x 20 mm samples from the thin sheets and annealed at 950 $^{\circ}\text{C}$ for 50 min in Ar / 2.5% H_2 (4 ppm O_2) gas environment followed by quenching in de-ionised water. After annealing the samples were abraded on the sides with 1200 grit to remove air formed oxide films.

Insulated Cu wire was soldered to the samples designated for electrochemical experiments and mounted in epoxy exposing the cross section. Long-cure epoxy kits obtained from Leco were used. The epoxy was mixed with a 100:14 resin to hardener ratio by weight and the curing time was 24 hrs at room temperature. After curing, the epoxy was ground to expose the sample cross-section and the samples were subsequently polished with 800 and 1200 grit sheets. The samples were cleaned with de-ionised water after polishing and introduced into the electrochemical cell immediately.

3.3. Preparation of Electrolyte

An equimolar (0.05 M / 0.05 M) acetic acid / sodium acetate buffer at pH = 4.67 was used for all experiments. The solutions were prepared from de-ionised water (with a conductivity of 18.2 MΩ-cm). AnalR[®] grade glacial acetic acid, CH₃COOH, (99.8% purity) from EMD and ACS grade sodium acetate tri-hydrate, CH₃COONa.3H₂O, (99% purity) from Alfa Aesar were used to prepare the buffer solution. 250 ml of the buffer was prepared by mixing 12.5 ml 1 M CH₃COOH solution and 1.701 g sodium acetate tri-hydrate in 237.5 ml de-ionised water. All pH and molarities mentioned are measured at room temperature. The pH of the solution was checked with a digital pH meter from Denver Instruments. The solution would be referred to as acetate buffer.

3.4. Electrochemistry

All the electrochemical experiments on Fe, Fe – 8% Cr and Fe – 10% Cr samples were carried out in a double walled glass cell with openings for a three electrode system and de-aeration. Water was filled in between the double walls to minimize effects from fluctuations in surrounding temperature. All experiments were carried out at room temperature. The solution was de-aerated using high purity N₂ gas (99.998%, O₂ < 3ppm) with the help of glass frit to promote dispersion within the electrolyte. The glass frit was raised above electrolyte level just before immersing the working electrode to avoid agitation; and de-aeration was carried out throughout the experiment. The solution was de-aerated for at least 30 min before sample introduction.

Pt wire was used as counter electrode. Before each experiment it was cleaned in 0.25 M HNO₃ solution by applying 2.1 V against Ni alloy cathode using a DC power supply.

Mercury / mercurous sulphate / satd. K_2SO_4 (MSE) was used as reference electrode. The MSE electrode measured 0.4 V vs. SCE and 0.64 V vs. NHE. All potentials are mentioned with respect to MSE. All the DC electrochemical studies were carried out using a Gamry Femtostat (FAS 2), software controlled electrochemical system.

Both Fe and Fe – Cr samples were cathodically pre-treated at -1.4 V for 1 min in the solution for removal of air formed oxides before each experiment. H_2 bubbles formed on surface during reduction were removed by tapping the sample just before stepping the potential to required values.

For experiments on Fe wire, the sample was potentiostatically polarized at -0.3 V for 30 min to form a passive layer followed by potentiodynamic polarization until -0.65 V at a scan rate of 1 mV/s. In another set of experiments on Fe wire, steady state polarization was carried out instead of a continuous potential sweep. Steady state current densities were measured at -0.4 V, -0.5 V and -0.6 V after potentiostatic polarization at each potential for 90 min, in separate experiments on samples passivated at -0.3 V for 30 min. Except at -0.6 V where Fe reactivation led to rapid increase in current density, steady state was reached well within 60 min.

All experiments on Fe microelectrode are corrected for IR drop based on Newman's equation for resistance to flow of current on a disk (57). Acetic acid being a very weak acid, electrical conductivity of the solution is assumed to be entirely from sodium acetate dissociation. The molar electrical conductivity of 0.05 M sodium acetate at 25°C and 1 atm. is $76.88 \text{ S.cm}^2.\text{mol}^{-1}$ (58), yielding the resistivity of solution as 260.15 $\Omega\text{-cm}$. The IR drop on a wire electrode is given by the equation below:

$$IR \text{ drop} = \rho \cdot a \cdot i \cdot \left(\frac{\pi}{4}\right)$$

where, a – Radius of wire (cm)

i – Current density (A/cm²)

ρ – Resistivity ($\Omega \cdot \text{cm}$)

In the case of experiments on Fe – Cr alloys, improvement of their resistance at very negative potentials by potential cycling was studied. For this purpose, potential in a square wave form was applied which is illustrated below.

Figure 2: Potential in square wave form applied before passivation during cycling experiments.

During potential cycling, the potential is alternately stepped between passivation and activation of Fe – Cr alloy for fixed number of cycles. The passivation and activation potential are designated as E_p and E_a in the illustration. One passivation and one activation step together are termed as one cycle here.

During potential cycling experiments, the square wave form of the potential was not applied as a pulse but was applied using user defined scripts in the Gamry Femtostat. It was ensured that, while stepping between passivation and activation potentials, potential control was not lost.

In the experiment, samples were passivated at -0.3 V for 30 min and followed by either potentiodynamic polarization or steady state polarization. Prior to the 30 min passivation, samples were polarized by potential cycling between E_p and E_a for 5 cycles or potentiostatically at E_p for the same duration as spent in 5 cycles. The potentiodynamic polarization was carried out from -0.3 V to -0.65 V at a scan rate of 0.1 mV/s. For steady state polarization, steady state current densities were measured at -0.4 V, -0.5 V and -0.6 V after holding potential for 1 hr, in separate experiments.

4. RESULTS AND DISCUSSIONS

4.1. Electrochemistry of Fe – 8% Cr alloys in 4.67 pH acetate buffer

The premise of this study is based on the hypothesis that alternately passivating Fe – Cr surface and activating it, by selectively dissolving Fe from the surface, several times should enrich the surface with Cr; and resulting in a better passivation state. In lieu with this, potentials for passivation and activation of Fe – Cr alloys from passive state in acetate buffer were determined. Acetate buffer was chosen for this study as it is very mildly acidic. Acetate buffer with pH very close to its pKa value of 4.75 and low concentration of acetate ions (0.1M) was used. Low concentration of acetate ions was chosen to avoid complexation effects (40). Also very mildly acidic pH was chosen to avoid possible Cr dissolution, which will be elaborated later.

4.1.1. Potential E_p for passivation

Figure 3 shows cyclic polarization of cathodically pre-treated Fe – 8% Cr sample between -1.0 V and 0.2 V at a scan rate of 1 mV/s in acetate buffer. The active – passive transition and passivity are clearly evident from anodic polarization. It can be observed from the plot that passivation starts to set-in from -0.8 V with complete passivation starting at -0.4 V and extending over a long potential range until 0.8 V. From another experiment, in which polarization was carried out over a wider potential range, graph not shown, transpassive dissolution and oxygen evolution was observed to start beyond 0.825 V. From the polarization curve, -0.3 V vs. MSE in passive region was chosen for passivation.

Figure 3: Cyclic polarization of Fe – 8% Cr between -1.0 V and 0.2 V vs. MSE in 4.67 pH acetate buffer.

4.1.2. Potential E_a for activation by selective dissolution of Fe

From the literature, it is well known that Fe – Cr alloys on passivation forms iron (III) and chromium (III) compounds on the surface. The dissolution of oxide films on Fe surface in acidic media was studied by Pryor and Evans (22). They identified it to be a reductive dissolution mechanism, generally represented by the following reaction

This holds for iron oxides formed on Fe – Cr alloys too. Several studies have shown Cr enrichment in passive film formed on Fe – Cr alloys to be a result of selective removal of Fe^{3+} ions from the surface into solution as Fe^{2+} ions by reductive dissolution (6-8, 12, 13).

Reductive dissolution occurs at the reactivation potential. There are several opinions on reactivation potential though. The most straight forward is that of Davenport et al. (1). They define reactivation for passivated Fe – Cr alloys as a state in which the open circuit potential drops to a value where ferric ions are reductively dissolved as ferrous ions into the solution along with simultaneous anodic dissolution of any exposed metallic iron. Fujimoto et al. (16) define reactivation potential as the potential at which current density increases anodically at the slightest onset of hydrogen evolution while polarizing towards less noble potentials from passive state.

Kirchheim et al. (7) passivated Fe – x% Cr alloys (x: 0.6% to 18%) for a fixed duration and subjected them to potentiodynamic polarization in less noble direction. The potential at which current density reached mid-value between maximum current density at active state and minimum at passive state was defined as reactivation potential. They also showed that above 12% Cr in the alloy there is no reactivation with the current increasing only cathodically. Since we were concerned more about low Cr content alloys efforts to replicate those results were not undertaken in this study.

To be clear, reactivation and activation as mentioned in this study are two different terms. Reactivation is an inherent property of the metal or alloy and very specific to its environment. Activation potential for the square wave polarization is chosen around this reactivation potential to enable exclusively Fe dissolution without Cr dissolution.

With regard to the present hypothesis, E_a during potential cycling should be in a potential range at which Cr continues to passivate and should be slightly cathodic to Fe – Cr reactivation potential. So that during potentiostatic polarization at E_a , only ferric ions are removed by reductive dissolution but new Cr atoms as exposed by selective dissolution continue to passivate. Figure 4 illustrates the whole process.

Figure 4: Illustration of the cycling process.

During initial passivation a mixed oxide of iron (III) compounds (white space) and chromium (III) compounds (Black dots) are formed on the surface. On stepping to activation potential, iron oxide at the film/solution interface is lost to the solution as Fe^{2+} ions by reductive dissolution and metal substrate gets exposed, but initially formed Cr^{3+} compounds remain intact on the surface. From the exposed surface, Fe dissolves into solution and Cr oxidises (White dots). Again stepping to passive potential leads to oxidation of both Fe and

Cr at the metal/film interface. Possibly some Fe^{2+} ions from solution get anodically deposited onto the surface during both activation and passivation.

Cr is known to passivate at very negative potentials. From Pourbaix diagram shown below in Figure 5 and Figure 6 it can be seen that stability of $\text{Cr}(\text{OH})_3$ and Cr_2O_3 extends till very negative potentials of ca. -0.6 V vs. SHE (-1.24 V vs. MSE) at pH 4.7. And previous studies have shown that Cr dissolution occurs below -0.3 V vs. SCE (-0.7 V vs. MSE) in 1 M sulphuric acid solution (59).

Figure 5: Potential – pH equilibrium diagram for the system chromium – water, at 25°C [Figure established considering $\text{Cr}(\text{OH})_3$] (24).

Figure 6: Potential – pH equilibrium diagram for the system chromium – water, at 25°C
[Figure established considering Cr_2O_3] (24).

This justifies, as mentioned earlier, the selection of such mildly acidic pH to prevent Cr oxide dissolution during activation step of potential cycling. So E_a can be chosen anywhere between -1.24 V and 0.15 V vs. MSE, safely without any ambiguity regarding Cr dissolution.

To determine the reactivation potential of Fe – 8% Cr alloys in acetate buffer, samples were passivated at -0.3 V for 30 min and subjected to potentiodynamic polarization till -1.0 V at different scan rates of 10 and 30 mV/s. Figure 7 shows the curves obtained during the initial passivation.

Figure 7: Passivation of Fe – 8% Cr at -0.3 V vs. MSE for 30 min in acetate buffer. Two samples A and B were passivated and polarized cathodically at scan rate of 10 and 30 mV/s respectively.

Figure 8 shows the potentiodynamic polarization at different scan rates from passive state. It can be seen that the peak current density decreases with increase in scan rate. This is probably because at high scan rates sufficient time is not available for complete removal of

the surface oxides which results in relatively lesser exposed Fe for dissolution. The current density starts to increase anodically from ca. -0.65 V vs. MSE at a scan rate of 30 mV/s and shifts towards positive potentials with decrease in scan rate. The current density becomes anodic at -0.58 V vs. MSE at 10 mV/s scan rate. Also in the cyclic polarization shown in Figure 3, it can be noticed in the back scan that the current density tends to become anodic from -0.58 V vs. MSE.

Figure 8: Potentiodynamic polarization of Fe – 8% Cr at scan rates of 10 and 30 mV/s after passivation at -0.3 V vs. MSE for 30 min in acetate buffer.

To eliminate the effect of scan rate, steady state current densities were determined at potentials of -0.45, -0.5, -0.55 and -0.6 V vs. MSE instead of potentiodynamic polarization.

Steady state current densities were measured by holding potential for 15 min. Figure 9 shows the steady state polarization of Fe – 8% Cr from passive state. The current density shows a minimum at -0.5 V vs. MSE and is taken as the reactivation potential of Fe – 8% Cr in 4.67 pH acetate buffer. So -0.5 V was used as activation potential, E_a during potential cycling. Also -0.6 V vs. MSE, slightly cathodic to reactivation potential was tried as activation potential E_a in some experiments for comparison.

Figure 9: Steady state polarization of Fe – 8% Cr from an initial passive film formed at -0.3 V vs. MSE for 30 min. Steady state current densities were measured by potentiostatic polarization at -0.45, -0.5, -0.55 and -0.6 V vs. MSE for 15 min.

4.2. Reactivation potential of Fe

While holding potential at E_a , for activation of Fe – Cr samples during the cycling experiments, it is Fe which is actually reactivated. So reactivation potential of Fe was determined in acetate buffer.

4.2.1. Cyclic polarization of Fe in acetate buffer

Figure 10 below shows cyclic polarization of Fe. The active and passive regions for Fe in acetate buffer are clearly visible from the voltammetry.

Figure 10: Cyclic polarization of Fe between -1.0 V and 0.2 V vs. MSE in 4.67 pH acetate buffer.

In the backward scan, the sample shows transition between cathodic and anodic behaviour for over 100 mV between -0.4 V to -0.52 V. The forward scan shows passivity to extend from -0.3 V till 0.2 V for Fe in pH 4.67 acetate buffer. From literature it is known to extend even further until start of transpassivity at ca. 0.6 V vs. MSE in pH 7 acetate buffer (60).

4.2.2. Determination of Fe reactivation potential

To determine the reactivation potential, same procedures as in Fe – Cr samples were followed. From the voltammetry shown in Figure 10, -0.3 V was chosen as passivation potential. Since during potential cycling, the total time spent on passivation and activation would amount to 195 min for 5 cycles, the effect of passivation time on Fe reactivation was checked. The samples were passivated for 30 and 195 min and then polarized at 0.1 mV/s till -0.65 V. The passivation curves are shown in Figure 11.

Figure 11: Passivation of Fe in acetate buffer at -0.3 V vs. MSE for different durations of 30 and 195 min, prior to potentiodynamic polarization at 0.1 mV/s till -0.65 V vs. MSE

Figure 12 below shows the polarization from passive state. Since 0.1 mV/s is a very slow scan rate, steady state current densities were not determined in the polarization range. As can be seen the reactivation potential is independent of passivation duration. The current density increases anodically at ca. -0.37 V. So -0.4 V was also used as activation potential, E_a during potential cycling. But the Fe – 8% Cr samples did not actually activate at -0.4 V as will be shown later. The current densities at the end of each activation step during potential cycling were always below passivation current density obtained just prior to start of activation step. The Cr prevents Fe reactivation true to its purpose of addition to the alloy

and shifts the reactivation potential more negative. The effect of Cr on Fe reactivation is discussed later in Figure 19.

Figure 12: Potentiodynamic polarization of Fe in acetate buffer from passive state created by potentiostatic polarization at -0.3 V vs. MSE for different durations of 30 and 195 min.

4.3. Cycling experiments

Potential cycling has been carried out by several authors previously. As mentioned earlier, Davenport et al. (12) cycled between multiple potential steps to study transpassive dissolution of Cr^{6+} . Mansfeld (51-54) and Fujimoto (55, 56) formed passive films on Type 304 stainless steel by applying a square wave pulse polarization. Mansfeld et al. were interested in forming better corrosion resistant films, while Fujimoto et al. were interested in forming thick films showing interference colours for aesthetic appeal.

In this present study, potential cycling has been employed to make low Cr alloys to act as stainless steel. Both passivation potential (E_p) and activation potential (E_a) for potential cycling illustrated in Figure 2 (corresponding to E_H and E_L mentioned in the study by Fujimoto et al. (56)) has been chosen in the passive region of Cr at pH 4.7. In the study carried by Fujimoto et al., Cr was removed from the surface as Cr^{2+} or Cr^{6+} in one step and then anodically oxidized or cathodically reduced to Cr^{3+} in the next step. But by choosing both potentials in passive region, Cr is continually oxidized on surface, the difference between the steps being caused by Fe passivation as Fe^{3+} in one step and removal as Fe^{2+} by reductive dissolution in the next step. The Fe and Cr Pourbaix diagrams are superimposed and given below in Figure 13 for comparison of oxide stability regions at pH 4.7. It should be noticed that Cr^{3+} is stable at both E_p and E_a , but Fe^{3+} is stable only at E_p and Fe^{2+} is the thermodynamically preferred state at E_a .

Figure 13: Superimposed Potential – pH equilibrium diagram for the system iron – water [considering Fe_2O_3] and chromium – water [considering $\text{Cr}(\text{OH})_3$] (shaded area) at 25°C (24).

4.3.1. Effect of potential cycling on Fe – Cr reactivation from passive state

To study the effect of potential cycling, two samples were passivated at -0.3 V for 30 min. Before the passivation, one sample was polarized potentiostatically at $E_p = -0.3$ V for 165 min and the other by potential cycling for 5 cycles with $E_p = -0.3$ V for 30 min, $E_a = -0.5$ V for 3 min (Total time = 165 min).

Figure 14 and Figure 15 below shows the formation of passive film without and with prior potential cycling.

Figure 14: Passivation of Fe – 8% Cr in acetate buffer at -0.3 V vs. MSE for 30 min with prior potentiostatic polarization at -0.3 V vs. MSE for 165 min (No potential cycling).

Figure 15: Passivation of Fe – 8% Cr in acetate buffer at -0.3 V vs. MSE for 30 min with prior polarization by potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).

Samples were polarized for the same duration before passivation – 165 min by either potentiostatic polarization or potential cycling; to eliminate doubts that potential cycling causes reduction in passivation current density just because of the longer duration elapsed during cycling experiments.

The effectiveness of passive film thus formed was inferred from their resistance to reactivation of the underlying metal. For this purpose the passive films formed without and with potential cycling were subjected to potentiodynamic polarization at a scan rate of

0.1 mV/s. The potentiodynamic polarization is shown below in Figure 16, and it can be seen that samples are relatively more passive when formed with prior potential cycling.

Figure 16: Potentiodynamic polarization of Fe – 8% Cr from passive state formed with two different prior treatments: Potentiostatic polarization at -0.3 V vs. MSE for 165 min with no cycling, Polarization by potential cycling ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min) for 5 cycles.

Also the current density at negative potentials is lower when the sample was subjected to potential cycling. This shows that the passive film formed by potential cycling is more robust and does not dissolve immediately by reductive dissolution, possibly because of an increase in degree of Cr enrichment during potential cycling. Whereas in a passive film

formed in one step as in the case of passivation without potential cycling, Fe dissolution occurs through the film as 8% Cr is probably not sufficient to form a continuous passive film.

4.3.2. Effect of number of cycles

To determine the effect of number of cycles, samples were subjected to potential cycling with 10 cycles. The current density plot during potential cycling for 10 cycles is shown in Figure 24 in Appendix. This resulted in better passivity than potential cycling for 5 cycles. But this could be due to the longer time spent during cycling for 10 cycles (330 min) as against 5 cycles (165 min). To elucidate more on this, the final current densities after i^{th} passivation and activation step during potential cycling for 10 cycles have been plotted with the number of cycle i as shown in Figure 17. It can be seen that the passivation current density is decreasing continually with each cycle implying consistent improvement. Also the activation current density is decreasing with each cycle which could possibly mean availability of lesser number of sites for Fe dissolution implying increased surface coverage by chromium oxide/hydroxide. It should be noted that activation current density is higher at the end of each activation step compared to previous passivation step confirming actual activation of the surface.

Figure 17: Final current densities of each passivation and activation step during potential cycling for 10 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).

4.3.3. Effect of variation in E_a on Fe – Cr reactivation from passive state

In the results presented so far, reactivation potential of Fe – Cr in acetate buffer measured as -0.5 V vs. MSE was used as activation potential, E_a , during potential cycling. Proceeding with the same line of thought presented so far, if reductive dissolution of Fe^{3+} from surface into solution as Fe^{2+} at reactivation potential leads to a more robust Cr enriched passive film, using an activation potential cathodic to reactivation potential during potential cycling should accelerate reductive dissolution leading to a relatively higher Cr enrichment on the surface.

To verify this, -0.4 V and -0.6 V vs. MSE were used as E_a during potential cycling, which are relatively anodic and cathodic to reactivation potential respectively.

Figure 18: Comparison of steady state polarization of Fe – 8% Cr from passive film formed at -0.3 V vs. MSE for 30 min with prior potential cycling ($E_p = -0.3$ V vs. MSE for 30 min; $E_a = -0.4$ V, -0.5 V and -0.6 V vs. MSE for 3 min) along with passive film formed with prior potentiostatic polarization at $E_p = -0.3$ V vs. MSE for 165 min. Steady state current densities were measured at -0.4 V, -0.5 V and -0.6 V vs. MSE after holding potential for 60 min.

Figure 18 compares the steady state polarization of Fe – 8% Cr from passive state with and without prior potential cycling. During potential cycling three different E_a values of

-0.4 V, -0.5 V and -0.6 V were used. The potential cycling for all experiments involved in obtaining the plot in Figure 18 are shown from Figure 25 to Figure 36 in Appendix.

From the plot it can be seen that using activation potential anodic to reactivation potential of Fe – Cr alloy during potential cycling is actually making the passive film less resistant leading to higher current densities at negative potentials compared to films formed even without cycling. With $E_a = -0.6$ V which is cathodic to reactivation potential, the resistance of passive film is better compared to that formed with $E_a = -0.5$ V during cycling. This adds credibility to the relatively rapid removal of Fe from surface leading to relatively higher Cr enrichment theory. It is interesting to note that, the steady state polarization from passive state obtained without cycling and with $E_a = -0.4$ V during cycling changes slope at the reactivation potential. Whereas the ones obtained with $E_a = -0.5$ V and -0.6 V during cycling have uniform slope throughout. This possibly signifies the change in mechanism at reactivation potential, i.e., onset of reductive dissolution of ferric ions into solution as ferrous ions.

4.3.4. Effect of Cr content on Fe reactivation

It can be seen in Figure 18 that there is not much improvement in the resistance of Fe – 8% Cr after reactivation during steady state polarization from passive state formed with cycling at $E_a = -0.5$ V and -0.6 V as compared to without cycling. The current density at -0.6 V of the steady state polarization decreased only by 24% for $E_a = -0.5$ V during potential cycling and 33.5% in the case of $E_a = -0.6$ V as compared to the current density obtained without cycling. The current density actually increased by 22% in the case of $E_a = -0.4$ V. No dramatic reduction in current densities in orders of magnitude was seen. This could possibly

be due to an insufficient time being spent on potential cycling procedure or due to an insufficient Cr content in the alloy to achieve required Cr enrichment on the surface. In lieu with this, the effect of Cr content was studied using Fe – 10% Cr.

Prior to studying the performance of Fe – 10% Cr alloy under potential cycling, the effect of Cr on Fe reactivation was studied. This was to determine reactivation potential in the case of Fe – 10% Cr in acetate buffer and to compare it with reactivation potential of Fe – 8% Cr. Figure 19 shows potentiodynamic polarization of Fe, Fe -8% Cr and Fe – 10% Cr in acetate buffer from passive state.

Figure 19: Potentiodynamic polarization of Fe, Fe – 8% Cr and Fe – 10% Cr from passive state formed by passivation at -0.3 V vs. MSE for 30 min in acetate buffer.

It can be seen that reactivation potential of Fe – 8% Cr and Fe – 10% Cr are the same. But rate of Fe dissolution after reactivation is decreased with an increase in Cr content as can be seen from the reduced current densities.

4.3.5. Effect of Cr content on cycling

To study the effect of Cr content on potential cycling, Fe – 8% Cr and Fe – 10% Cr samples were passivated at -0.3 V for 30 min with prior potential cycling ($E_p = -0.3$ V for 30 min, $E_a = -0.6$ V for 3 min) for 5 cycles and steady state current density was measured at -0.6 V after holding potential for 1 hr. This is also compared with steady state current densities measured at -0.6 V for Fe – 8% Cr and Fe – 10% Cr samples passivated without potential cycling. The potentiostatic polarization curves for the above mentioned experiments are shown in Figure 20. The current density measurements during potential cycling for Fe – 10% Cr samples are given in Figure 37 and Figure 38 in the Appendix.

It can be seen from the plot that potential cycling improves the resistance to metal dissolution at potentials cathodic to reactivation potential for both 8% and 10% Cr alloys. Also the degree of resistance increases with increase in Cr content. The steady state current density measured on Fe – 10% Cr is almost one-fifth of that measured on Fe – 8% Cr after both were subjected to potential cycling.

Figure 20: Potentiostatic polarization of Fe – 8% Cr and Fe -10% Cr at -0.6 V vs. MSE for 1 hr. Samples were passivated at -0.3 V vs. MSE for 30 min with prior polarization by either potential cycling ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min) or potentiostatic polarization at -0.3 V vs. MSE for 165 min, before measurement of steady state current density.

4.4. Thermodynamic control of Fe reactivation in acetate buffer

During the determination of reactivation potential for Fe in acetate buffer, it was observed that Fe reactivation follows an inverted Tafel behaviour as seen in Figure 12. This could possibly mean a thermodynamic control on Fe reactivation. Since Fe reactivation occurs by reductive dissolution of Fe^{3+} oxides/oxyhydroxides into solution as Fe^{2+} ions, the

thermodynamic control could possibly mean a mass transport control based on diffusion of Fe^{2+} ions into the bulk.

To verify the mass transport control, a simple experiment was performed in which stirring was turned on intermittently during potentiodynamic polarization from passive state.

Figure 21: Potentiodynamic polarization from passive state formed by potentiostatic polarization at -0.3 V vs. MSE for 30 min, with stirring turned on and off for very short instances at random potentials.

Figure 21 above shows the results from stirring experiment and it can be seen that current density increases and decreases upon stirring, indicating a degree of mass transport

control on Fe reactivation by reductive dissolution. The results have been presented in both linear and logarithmic scale to make the effects of stirring more apparent.

4.4.1. Comparison of theoretically calculated Nernstian lines with experimental potentiodynamic polarization and steady state polarization

Though the chemical structure of the passive film on Fe is widely accepted to be made of $\gamma - \text{Fe}_2\text{O}_3$ or $\gamma - \text{FeOOH}$, they are not scientific facts yet. But the ability of Nernst equation to establish thermodynamic equilibrium between various ferric oxides / hydroxides / oxyhydroxides and ferrous ions is beyond questioning. Capitalizing on the thermodynamic control of Fe reactivation by reductive dissolution, limiting current density based on mass transport control along with Nernst equation can be utilized to construct theoretical potential – current density curves; which when compared with experimental potentiodynamic polarization curves could shed light on chemical structure of the passive film formed under specific conditions.

The various Fe^{3+} species that can possibly be formed on the surface during passivation are $\alpha - \text{Fe}_2\text{O}_3$, $\gamma - \text{Fe}_2\text{O}_3$, $\alpha - \text{FeOOH}$, $\gamma - \text{FeOOH}$ and $\text{Fe}(\text{OH})_3$. The reductive dissolution of these ferric species can be represented by the Nernst equation given below. The reduction reaction for each species is shown in Table 1.

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - 0.1773\text{pH} - 0.0591\log[\text{Fe}^{2+}]$$

where, $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ – Equilibrium potential

$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0$ – Standard equilibrium potential

$[\text{Fe}^{2+}]$ – Concentration of Fe^{2+} ions at equilibrium

The standard equilibrium potential is determined from standard free energy of formation (ΔG_f^o) of the Fe^{3+} species by the relation,

$$E_{Fe^{3+}/Fe^{2+}}^o = -\frac{\Delta G_{rxn}}{nF}$$

where, ΔG_{rxn} – Free energy of formation for the reduction reaction

$$\Delta G_{rxn} = \sum \Delta G_f^o_{products} - \sum \Delta G_f^o_{reactants} \text{ of reduction reaction}$$

n – Number of electrons involved in the reduction reaction

F – Faraday's constant

Table 1: Standard equilibrium potentials for different Fe^{3+}/Fe^{2+} reduction reactions

Equilibrium Reduction Reactions	Phase	ΔG_f^o (kJ/mol)	ΔG_{rxn} (kJ/mol)	$E_{Fe^{3+}/Fe^{2+}}^o$ (V vs. SHE)
$Fe_2O_3 + 6H^+ + 2e^- \leftrightarrow 2Fe^{2+} + 3H_2O$	$\alpha - Fe_2O_3$	-744.30 ⁽⁶¹⁾	-128.02	0.66
	$\gamma - Fe_2O_3$	-727.90 ⁽⁶²⁾	-144.42	0.75
$FeOOH + 3H^+ + e^- \leftrightarrow Fe^{2+} + 2H_2O$	$\alpha - FeOOH$	-489.80 ⁽⁶²⁾	-65.46	0.68
	$\gamma - FeOOH$	-480.10 ⁽⁶²⁾	-75.16	0.78
$Fe(OH)_3 + 3H^+ + e^- \leftrightarrow Fe^{2+} + 3H_2O$	$Fe(OH)_3$	-694.54 ⁽⁶³⁾	-98.12	1.02

In the determination of ΔG_{rxn} , standard free energy of formation for Fe^{2+} and H_2O were used as -78.86 and -238.2 kJ/mol respectively (63).

The equilibrium concentration of Fe^{2+} ions, $[\text{Fe}^{2+}]$ is determined from the diffusion controlled limiting current density given by,

$$i_{lim} = \frac{nFDC_{eq}}{h}$$

where, i_{lim} – Limiting current density (A.cm^{-2})

D – Diffusion coefficient of reacting species ($\text{cm}^2.\text{s}^{-1}$)

C_{eq} – Equilibrium concentration of reacting species (M)

h – Boundary layer thickness (cm)

The boundary layer thickness, h was determined from limiting current density for oxygen reduction on Pt wire ($d = 375 \mu\text{m}$) in pH 4.67 acetate buffer under aerated conditions. The Pt working electrode used for this experiment was carefully chosen to have same geometry as Fe microelectrode used in this study. Pt wire mounted in epoxy with its cross-section exposed was used.

Figure 22 below shows potentiodynamic polarization of Pt in aerated acetate buffer with current being limited by oxygen diffusion between -0.3 V and -0.9 V vs. MSE beyond which current again increases due to hydrogen evolution.

The 100% saturation concentration of O_2 in water at 25°C , 1 atm pressure is 8.6 ppm (64). This ppm value corresponds to a molar concentration of $2.68 \times 10^{-4} M$. Assuming $C_{eq} = 2.68 \times 10^{-4} M$ along with $D_{\text{O}_2} = 2.5 \times 10^{-5} \text{ cm}^2/\text{s}$ (65), $n = 4$ for oxygen reduction and $i_{lim} = 130 \mu\text{A}/\text{cm}^2$ from Figure 22; boundary layer thickness is calculated as 0.0199 cm .

Figure 22: Potentiodynamic polarization of Pt in pH 4.67 acetate buffer

For the different Fe^{3+} species, at particular equilibrium potentials, $[\text{Fe}^{2+}]$ is determined at $\text{pH} = 4.67$ using Nernst equation, from which i_{lim} is determined using limiting current equation and theoretical $E_{\text{Fe}^{3+}/\text{Fe}^{2+}} \text{ vs. } i_{lim}$ lines are plotted. For the determination of i_{lim} , $D_{\text{Fe}^{2+}} = 2 \times 10^{-5} \text{ cm}^2/\text{s}$ (66) and $h = 0.0199 \text{ cm}$ was used. The theoretically calculated data are shown in Table 2 in the Appendix.

These lines are compared with experimental Fe reactivation curve obtained by potentiodynamic polarization from passive state formed at -0.3 V vs. MSE for 30 min. To eliminate doubts on scan rate, steady state polarization curve is also plotted with steady state current densities measured at -0.4 V , -0.5 V and -0.6 V vs. MSE after potentiostatically

polarizing at each potential for 2500 sec. (In the experiments to determine steady state polarization, samples were potentiostatically polarized for 1 hr, but at -0.6 V vs. MSE the current increased very rapidly towards the end and pits were visible on examination of the sample after removing from solution. So the steady state current density was taken at 2500 sec for all three potentials).

Figure 23 below shows the comparison between experimental potentiodynamic polarization and steady state polarization with theoretically calculated potential – current density data. From the plot it can be observed that α and γ forms of the oxide and oxyhydroxide pair up to display very close equilibrium properties and also γ forms agree better than α form with the experimental data. This agrees well with previous studies in which $\gamma - \text{Fe}_2\text{O}_3$ and $\gamma - \text{FeOOH}$ are the most accepted chemical structure of passive film.

Recently Tromans (67) has shown that standard free energy of formation of a substance depends on its crystallinity. He has estimated an increase of 95.5 and 81.1 kJ/mol in free energy of formation of $\alpha - \text{Fe}_2\text{O}_3$ and $\gamma - \text{Fe}_2\text{O}_3$ for a 100% phase transformation from crystallinity to amorphism. He has quantified free energy of formation for fully amorphous oxide and partial amorphous oxide as

$$(\Delta G_f^\circ)_a = (\Delta G_f^\circ)_c + \Delta G_{a-c}$$

$$\left[(\Delta G_f^\circ)_a \right]_{\text{partial}} = (\Delta G_f^\circ)_c + \phi \Delta G_{a-c}$$

where, $0 < \phi < 1$ $\begin{cases} \phi = 0 \Rightarrow 100\% \text{ amorphous phase} \\ \phi = 1 \Rightarrow 100\% \text{ crystalline phase} \end{cases}$

$(\Delta G_f^\circ)_a$ – Free energy of formation of fully amorphous phase

$(\Delta G_f^\circ)_c$ – Free energy of formation of fully crystalline phase

$\left[(\Delta G_f^\circ)_a\right]_{\text{partial}}$ – Free energy of formation of partially amorphous phase

ΔG_{a-c} – Difference in free energy of formation between fully crystalline and amorphous phase

Figure 23: Comparison of experimental polarization data (A: Potentiodynamic, B: Steady state) for Fe reactivation with theoretical data (C: $\alpha - \text{Fe}_2\text{O}_3$, D: $\gamma - \text{Fe}_2\text{O}_3$, E: $\alpha - \text{FeOOH}$, F: $\gamma - \text{FeOOH}$, G: $\text{Fe}(\text{OH})_3$ and H: 19.5% amorphous $\gamma - \text{Fe}_2\text{O}_3$) for equilibrium relation between the different Fe^{3+} species and Fe^{2+} ions.

Based on Tromans's relation, the experimental steady state polarization corresponds to 19.5% amorphous oxide in the case of $\gamma - \text{Fe}_2\text{O}_3$. Lack of data on enthalpy of fusion and melting temperature in the case of $\gamma - \text{FeOOH}$, which are prerequisite to determine ΔG_{a-c}

makes it difficult to estimate the percentage of amorphism that would explain its proximity to experimental data.

5. IMPLICATIONS AND FUTURE WORK

Surface modification forms the key to achieve highly corrosion resistant materials. Techniques such as Ion implantation, LASER treatment provide results that cannot be achieved by alloying. But their high cost and feasibility to treat only smaller areas, limits their application. Electrochemical techniques such as potential cycling mentioned in this study and some previous studies, are promising viable alternatives to achieve higher degree of corrosion resistance in industrial alloys.

This electrochemical work was mostly qualitative. Improvement in Fe – Cr alloy properties owing to potential cycling was inferred mainly from two parameters – Passivation current densities and Resistance to reactivation from passive state. According to Percolation model of Newman and Sieradzki, incomplete passivation of low Cr alloys should be associated with detachment of Cr clusters leading to discrepancies in mass loss and anodic charge passed (48). Monitoring Cr ion concentration in the solution would increase credibility of Percolation model for passivation. And subsequent termination of Cr dissolution during potential cycling would be evident of the hypothesis. Monitoring Fe^{2+} ion concentration as well, can possibly provide insights into passivation mechanism. Also in-situ analysis of the surface by techniques such as XPS, XANES, STM, AFM can provide quantitative information on composition and structure of passive film formed by potential cycling. Stability of the passive film can be determined by measuring time required for OCP to reach bare metal value. Further, stability of the film can be determined by subjecting it to standard corrosion tests.

Another assumption of Percolation model is that, Cr atoms in low – Cr alloys have to move from their lattice position, or structurally relax, to achieve infinite connectivity (17). This results in gel-like oxide layer during fast selective dissolution of Fe. But potential cycling should eventually result in sufficient concentration of Cr atom at the surface, capable of forming infinite network of –Cr–O–Cr– without movement of Cr atoms from their lattice position. In-situ AFM experiments, using Force Imaging mode, would be capable of capturing such transitions from gel-like structure to a more condensed Cr-rich film.

In this study, effects of varying activation potential during potential cycling and effect of Cr content were analyzed, on improvement in resistance of low Cr alloys at negative potentials. Further parameters such as ratio between passivation and activation time during potential cycling have to be studied for better understanding and optimization of the process. The passivation current density drops to very low values after potential cycling but still continues at constant values after few 100 seconds, indicating persistent dissolution through the oxide. Ideally, t^{-1} decay of passivation current density would be desirable, which may be obtained by optimization of the process parameters.

The threshold behaviour of Fe – Cr alloys is still a wide open subject. Understanding the mechanism why low Cr alloys result in better passivity with potential cycling might provide insights to understanding the threshold behaviour. Also, potential cycling adds another dimension to the Percolation model of passivity. The model requires Cr content of Fe – Cr alloy to be at a critical concentration, to achieve infinite connectivity between Cr atoms in the oxide film. So, it needs to be verified whether the model would still hold if critical concentration of Cr is attained after a certain definite period of time, starting from a lesser value.

Though the experiments on Fe microelectrode were simple, the inverted Tafel behaviour of Fe reactivation has opened new insights into the reactivation process itself. While the mass transport control on Fe reactivation was verified by simple stirring experiments, further validation can be obtained by using Rotating Disc Electrode (RDE). The nature of oxide film on the surface, controlling Fe reactivation has been estimated based on thermodynamic data from the literature. In-situ analysis can further strengthen these results.

6. CONCLUSIONS

1. The hypothesis that cycling through reactivation potential will continually enrich passive film, on low-Cr alloy, in Cr by selective dissolution of Fe has been verified electrochemically, based on reduction in passivation current densities and resistance to reactivation.
2. Reactivation potential of Fe, Fe – 8% Cr and Fe – 10% Cr in acetate buffer of pH 4.67 have been determined.
3. Activation potential, E_a , for potential cycling should be cathodic to reactivation potential of Fe – xCr ($x < 10\%$) alloy, as deleterious effects are clearly evident while choosing an activation potential anodic to reactivation potential.
4. The hypothesis that reactivation of iron from the passive state in mild acid is controlled by mass transport has been validated, with indirect evidence for the nature of the solid substance whose potential-dependent solubility by reductive dissolution controls such reactivation.

REFERENCES

1. A. J. Davenport, M. P. Ryan, M. C. Simmonds, P. Ernst, R. C. Newman, S. R. Sutton and J. S. Colligon, *Journal of the Electrochemical Society*, **148**, B217 (2001).
2. J. B. Lumsden and R. W. Staehle, *Scripta Metallurgica*, **6**, 1205 (1972).
3. A. E. Yaniv, J. B. Lumsden and R. W. Staehle, *Journal of the Electrochemical Society*, **124**, 490 (1977).
4. V. Mitrovicscepanovic, B. Macdougall and M. J. Graham, *Corrosion Science*, **24**, 479 (1984).
5. I. Olefjord and H. Fischmeister, *Corrosion Science*, **15**, 697 (1975).
6. K. Asami, K. Hashimoto and S. Shimodaira, *Corrosion Science*, **18**, 151 (1978).
7. R. Kirchheim, B. Heine, H. Fischmeister, S. Hofmann, H. Knote and U. Stolz, *Corrosion Science*, **29**, 899 (1989).
8. S. Haupt and H. H. Strehblow, *Corrosion Science*, **37**, 43 (1995).
9. V. Maurice, W. P. Yang and P. Marcus, *Journal of the Electrochemical Society*, **143**, 1182 (1996).
10. P. Keller and H. H. Strehblow, *Corrosion Science*, **46**, 1939 (2004).
11. M. Kerkar, J. Robinson and A. J. Forty, *Faraday Discussions*, 31 (1990).
12. A. J. Davenport, H. S. Isaacs, J. A. Bardwell, B. Macdougall, G. S. Frankel and A. G. Schrott, *Corrosion Science*, **35**, 19 (1993).
13. L. J. Oblonsky, M. P. Ryan and H. S. Isaacs, *Journal of the Electrochemical Society*, **145**, 1922 (1998).
14. R. Kirchheim, B. Heine, S. Hofmann and H. Hofsass, *Corrosion Science*, **31**, 573 (1990).
15. P. Monnartz, *Metallurgie*, **8**, 161 (1911).
16. S. Fujimoto, R. C. Newman, G. S. Smith, S. P. Kaye, H. Kheyrandish and J. S. Colligon, *Corrosion Science*, **35**, 51 (1993).

17. M. P. Ryan, R. C. Newman and G. E. Thompson, *Philosophical Magazine B-Physics of Condensed Matter Statistical Mechanics Electronic Optical and Magnetic Properties*, **70**, 241 (1994).
18. M. P. Ryan, R. C. Newman and G. E. Thompson, *Journal of the Electrochemical Society*, **141**, L164 (1994).
19. H. H. Uhlig, *Zeitschrift Fur Elektrochemie*, **62**, 700 (1958).
20. K. Sieradzki and R. C. Newman, *Journal of the Electrochemical Society*, **133**, 1979 (1986).
21. E. McCafferty, *Electrochemical and Solid State Letters*, **3**, 28 (2000).
22. M. J. Pryor and U. R. Evans, *Journal of the Chemical Society*, 1259 (1950).
23. H. G. Oswin and M. Cohen, *Journal of the Electrochemical Society*, **104**, 9 (1957).
24. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solution*, NACE (1974).
25. M. Nagayama and M. Cohen, *Journal of the Electrochemical Society*, **109**, 781 (1962).
26. M. Nagayama and M. Cohen, *Journal of the Electrochemical Society*, **110**, 670 (1963).
27. V. Markovac and M. Cohen, *Journal of the Electrochemical Society*, **114**, 674 (1967).
28. V. Markovac and M. Cohen, *Journal of the Electrochemical Society*, **114**, 678 (1967).
29. Hashimoto, K. and M. Cohen, *Journal of the Electrochemical Society*, **121**, 37 (1974).
30. M. Cohen, D. Mitchell and K. Hashimoto, *Journal of the Electrochemical Society*, **126**, 442 (1979).
31. C. L. Foley, J. Kruger and Bechtold, Cj, *Journal of the Electrochemical Society*, **114**, 994 (1967).
32. J. Kruger and J. P. Calvert, *Journal of the Electrochemical Society*, **114**, 43 (1967).
33. N. Sato, K. Kudo and T. Noda, *Corrosion Science*, **10**, 785 (1970).
34. N. Sato, K. Kudo and T. Noda, *Electrochimica Acta*, **16**, 1909 (1971).
35. J. A. Bardwell, B. Macdougall and M. J. Graham, *Journal of the Electrochemical Society*, **135**, 413 (1988).

36. M. P. Ryan, S. Fujimoto, G. E. Thompson and R. C. Newman, in *Passivation of Metals and Semiconductors*, K. E. Heusler Editor, p. 233, Transtec Publications Ltd, Zurich-Uetikon (1995).
37. A. J. Davenport and M. Sansone, *Journal of the Electrochemical Society*, **142**, 725 (1995).
38. A. J. Davenport, J. A. Bardwell and C. M. Vitus, *Journal of the Electrochemical Society*, **142**, 721 (1995).
39. L. J. Oblonsky, A. J. Davenport, M. P. Ryan, H. S. Isaacs and R. C. Newman, *Journal of the Electrochemical Society*, **144**, 2398 (1997).
40. K. Takahashi, B. Macdougall and M. J. Graham, *Journal of the Electrochemical Society*, **137**, 3023 (1990).
41. L. J. Oblonsky, M. P. Ryan and H. S. Isaacs, *Corrosion Science*, **42**, 229 (2000).
42. J. A. Bardwell, B. Macdougall, D. F. Mitchell and M. J. Graham, *Journal of the Electrochemical Society*, **137**, 3311 (1990).
43. J. A. Bardwell, *Corrosion Science*, **30**, 1009 (1990).
44. J. A. Bardwell, G. I. Sproule, D. F. Mitchell, B. Macdougall and M. J. Graham, *Journal of the Chemical Society-Faraday Transactions*, **87**, 1011 (1991).
45. J. A. Bardwell, G. I. Sproule and M. J. Graham, *Journal of the Electrochemical Society*, **140**, 50 (1993).
46. C. L. McBee and J. Kruger, *Electrochimica Acta*, **17**, 1337 (1972).
47. V. Maurice, W. P. Yang and P. Marcus, *Journal of the Electrochemical Society*, **141**, 3016 (1994).
48. R. C. Newman, F. T. Meng and K. Sieradzki, *Corrosion Science*, **28**, 523 (1988).
49. E. McCafferty, *Corrosion Science*, **42**, 1993 (2000).
50. E. McCafferty, *Journal of the Electrochemical Society*, **149**, B333 (2002).
51. L. Kwiatkowski and F. Mansfeld, *Journal of the Electrochemical Society*, **140**, L39 (1993).
52. F. Mansfeld, S. H. Lin and L. Kwiatkowski, *Corrosion Science*, **34**, 2045 (1993).
53. F. Mansfeld, S. H. Lin and L. Kwiatkowski, *Corrosion*, **50**, 838 (1994).

54. P. Schmuki, H. Bohni and F. Mansfeld, *Journal of the Electrochemical Society*, **140**, L119 (1993).
55. S. Fujimoto, T. Shibata, K. Wada and T. Tsutae, *Corrosion Science*, **35**, 147 (1993).
56. S. Fujimoto and T. Shibata, in *Passivation of Metals and Semiconductors*, K. E. Heusler Editor, p. 741, Transtec Publications Ltd, Zurich-Uetikon (1995).
57. J. Newman, *Journal of the Electrochemical Society*, **113**, 501 (1966).
58. R. C. Weast, in *Handbook of chemistry and physics*, 67 ed., p. D167 (1986 - 1987).
59. T. P. Moffat and R. M. Latanision, *Journal of the Electrochemical Society*, **139**, 1869 (1992).
60. K. Takahashi, J. A. Bardwell, B. Macdougall and M. J. Graham, *Electrochimica Acta*, **37**, 477 (1992).
61. B. S. Hemingway, *American Mineralogist*, **75**, 781 (1990).
62. J. Majzlan, K. D. Grevel and A. Navrotsky, *American Mineralogist*, **88**, 855 (2003).
63. R. M. Cornell and U. Schwertmann, *The Iron Oxides: Structures, Properties, Reactions, Occurences and Uses*, WILEY - VCH GmbH & Co. (2003).
64. B. H. Munson, R. Axler, C. Hagley, G. Host, G. Merrick and C. Richards, <http://waterontheweb.org/under/waterquality/oxygen.html>, in *Water on web*.
65. R. H. Perry and D. W. Green, in *Perry's Chemical Engineers' Handbook*, 7th ed., p. 2/332, McGraw-Hill (1997).
66. D. S. Azambuja and I. L. Muller, *Corrosion Science*, **36**, 1835 (1994).
67. D. Tromans, *Journal of the Electrochemical Society*, **152**, B460 (2005).

APPENDIX

Table 2: $\text{Fe}^{3+}/\text{Fe}^{2+}$ equilibrium potential vs. i_{lim} data for different Fe^{3+} species

$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ (V vs. MSE)	i_{lim} (A/cm ²)				
	$\alpha - \text{Fe}_2\text{O}_3$	$\gamma - \text{Fe}_2\text{O}_3$	$\alpha - \text{FeOOH}$	$\gamma - \text{FeOOH}$	$\text{Fe}(\text{OH})_3$
-0.15	-	-	-	-	1.07E-06
-0.20	-	-	-	-	7.53E-06
-0.25	-	-	-	-	5.28E-05
-0.30	-	-	-	-	3.70E-04
-0.35	-	-	-	-	2.60E-03
-0.40	-	7.56E-07	-	1.24E-06	1.82E-02
-0.45	-	5.30E-06	-	8.72E-06	-
-0.50	1.36E-06	3.72E-05	1.22E-06	6.12E-05	-
-0.55	9.52E-06	2.61E-04	8.55E-06	4.29E-04	-
-0.60	6.68E-05	1.83E-03	6.00E-05	3.01E-03	-
-0.65	4.68E-04	1.28E-02	4.21E-04	2.11E-02	-
-0.70	3.29E-03	-	2.95E-03	-	-
-0.75	2.31E-02	-	2.07E-02	-	-

Figure 24: Passivation of Fe – 8% Cr in acetate buffer at -0.3 V vs. MSE for 30 min with prior polarization by potential cycling for 10 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).

Figure 25: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.4 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).

Figure 26: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.5 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).

Figure 27: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.5$ V vs. MSE for 3 min).

Figure 28: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.4 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.4$ V vs. MSE for 3 min).

Figure 29: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.5 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.4$ V vs. MSE for 3 min).

Figure 30: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.4$ V vs. MSE for 3 min).

Figure 31: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.4 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min).

Figure 32: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.5 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min).

Figure 33: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min).

Figure 34: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.4 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior polarization at $E_p = -0.3$ V vs. MSE for 165 min (No cycling).

Figure 35: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.5 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior polarization at $E_p = -0.3$ V vs. MSE for 165 min (No cycling).

Figure 36: Potentiostatic polarization of passivated Fe – 8% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior polarization at $E_p = -0.3$ V vs. MSE for 165 min (No cycling).

Figure 37: Potentiostatic polarization of passivated Fe – 10% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior potential cycling for 5 cycles ($E_p = -0.3$ V vs. MSE for 30 min, $E_a = -0.6$ V vs. MSE for 3 min).

Figure 38: Potentiostatic polarization of passivated Fe – 10% Cr in acetate buffer at -0.6 V vs. MSE for 1 hr to measure steady state current density. Passive film was formed at -0.3 V vs. MSE for 30 min with prior polarization at $E_p = -0.3$ V vs. MSE for 165 min (No cycling).